PB 188 077

AIR POLLUTION ASPECTS OF SELENIUM AND ITS COMPOUNDS

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Litton Systems, Incorporated
Bethesda, Maryland

September 1969

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AIR POLLUTION ASPECTS

OF

SELENIUM AND ITS COMPOUNDS

Prepared for the
National Air Pollution Control Administration
Consumer Protection & Environmental Health Service
Department of Health, Education, and Welfare
(Contract No. PH-22-68-25)

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September 1969

FOREWORD

As the concern for air quality grows, so does the concern over the less ubiquitous but potentially harmful contaminants that are in our atmosphere. Thirty such pollutants have been identified, and available information has been summarized in a series of reports describing their sources, distribution, effects, and control technology for their abatement.

A total of 27 reports have been prepared covering the 30 pollutants. These reports were developed under contract for the National Air Pollution Control Administration (NAPCA) by Litton Systems, Inc. The complete listing is as follows:

Aeroallergens (pollens)
Aldehydes (includes acrolein and formaldehyde)
Ammonia
Arsenic and Its Compounds
Asbestos
Barium and Its Compounds
Beryllium and Its Compounds
Biological Aerosols (microorganisms)
Boron and Its Compounds
Cadmium and Its Compounds
Chlorine Gas
Chromium and Its Compounds (includes chromic acid)
Ethylene
Hydrochloric Acid
Hydrogen Sulfide
Iron and Its Compounds
Manganese and Its Compounds
Mercury and Its Compounds
Nickel and Its Compounds
Odorous Compounds
Organic Carcinogens
Pesticides
Phosphorus and Its Compounds
Radioactive Substances
Selenium and Its Compounds
Vanadium and Its Compounds
Zinc and Its Compounds

These reports represent current state-of-the-art literature reviews supplemented by discussions with selected knowledgeable individuals both within and outside the Federal Government. They do not however presume to be a synthesis of available information but rather a summary without an attempt to interpret or reconcile conflicting data. The reports are

necessarily limited in their discussion of health effects for some pollutants to descriptions of occupational health exposures and animal laboratory studies since only a few epidemiologic studies were available.

Initially these reports were generally intended as internal documents within NAPCA to provide a basis for sound decision-making on program guidance for future research activities and to allow ranking of future activities relating to the development of criteria and control technology documents. However, it is apparent that these reports may also be of significant value to many others in air pollution control, such as State or local air pollution control officials, as a library of information on which to base informed decisions on pollutants to be controlled in their geographic areas. Additionally, these reports may stimulate scientific investigators to pursue research in needed areas. They also provide for the interested citizen readily available information about a given pollutant. Therefore, they are being given wide distribution with the assumption that they will be used with full knowledge of their value and limitations.

This series of reports was compiled and prepared by the Litton personnel listed below:

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Appreciation is expressed to the many individuals both outside and within NAPCA who provided information and reviewed draft copies of these reports. Appreciation is also expressed to the NAPCA Office of Technical Information and Publications for their support in providing a significant portion of the technical literature.

ABSTRACT

Selenium compounds in the atmosphere are known to cause irritation of the eyes, nose, throat, and respiratory tract in humans, and under conditions of prolonged exposure, gastrointestinal disorders result. In animals there are indications that selenium ingestion may cause cancer of the liver, and it is known to produce pneumonia and degeneration of liver and kidneys.

Sources of atmospheric selenium include combustion of industrial and residential fuels, refinery waste gases and fumes, and incineration of wastes including paper products which contain as much as 6 ppm selenium. Little data is available on concentrations of selenium in the air; one report indicated an average value of 0.001 $\mu g/m^3$ in the vicinity of Boston, Mass.

Electrostatic precipitators and water scrubbers are effective in controlling emissions of selenium in industrial operations. No information has been found on the economic costs of selenium air pollution, or on the costs of its abatement. Methods are available for the analysis of selenium in the atmosphere.

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1. INTRODUCTION

Selenium poisoning of humans and animals from ingestion of foods containing toxic amounts of selenium has been and still is a problem of great concern in the United States. Many plants used as food by humans and animals can accumulate high concentrations of selenium from the soil. The soils of the Midwest are particularly high in selenium. Extensive studies have been made of the people, animals, food products, and soils of the high seleniferous areas. Selenium has also been found to be an essential nutrient for animals and may be necessary for humans.

Selenium compounds, although toxic, have seldom presented a serious problem in industry. Inhalation of the dust, fumes, or vapors of selenium compounds can irritate the eyes, nose, and throat, causing lacrimation, palpebral edema, conjunctivitis, sneezing, nasal congestion, anosmia, and coughing.

A study made in Boston, Mass. showed that there was approximately 0.001 $\mu g/m^3$ of selenium in samples of rain, snow, and air analyzed. The sources of atmospheric selenium are believed to be terrestrial, such as fuels and ores used by industry, or possibly the burning of trash, particularly paper.

2. EFFECTS

2.1 Effects on Humans

Little information is available on the toxicity of selenium through inhalation by humans. This is partly due to the infrequent occurrence of serious intoxication during the industrial use of selenium and its compounds, and also to the fact that human exposure is largely through the consumption of food.

Industrial exposures are commonly a result of inhalation of the dust, fumes, and vapors of selenium and its compounds, although ingestion and skin contact are also important. The effects of industrial exposure have been reported by Hamilton,[51,52] Dudley,[26,27] Amor and Pringle,[2] Clinton,[16] and Glover.[44] Discussion of these effects can be found in Trelease and Beath,[119] Cerwenka and Cooper,[12] Patty,[89] and Cooper.[19]

The effects of selenium and its compounds on humans appear to differ somewhat from those observed in animals. Thus, although animals can display definite disease responses to the amount of selenium ingested (see Section 2.2), there have been no chronic diseases in man attributable to selenium or its compounds.[44]

2.1.1 Chronic Effects

In general, chronic selenium intoxication in man produces the following symptoms: depression, marked pallor, coated tongue,

languor, nervousness, occasional dermatitis, gastrointestinal disturbances, giddiness, and garlic odor of the breath and sweat.[12,19,51] Moxon and Rhian[84] also noted small local hemorrhages, severe ascites, liver and splenic damage, emaciation, apathy, and progressive anemia. Hamilton[52] mentioned irritation of nose, throat, and bronchi; pain in the lumbar region; nasal inflammation resembling that accompanying a cold; and night sweats. The above authors believe that garlic odor of the breath is one of the earliest and most characteristic symptoms of selenium intoxication.[2,43] Although there has been some question whether trace impurities of tellurium may give the garlic odor,[89] this odor has been found in workers exposed to 99.999 percent pure selenium.[44] Other authors believe that symptoms of respiratory ailments and gastrointestinal disturbances are of major significance in the diagnosis of selenium poisoning.

Rosenfeld and Beath[97] stated that the possible long-term effects of selenium may be kidney and liver damage. Also fibrosis of the lung may develop following continued exposure to dust and gases in the air.

The studies of Hadjimarkos[47] and the data from earlier investigators[109,111] suggest that selenium can increase the susceptibility of humans to dental caries. However, Cadell and Cousins[11] found no changes in primary, decayed, missing, and

filled teeth that would indicate dependence on selenium intake.

Apparently the toxicity of selenium to humans may be somewhat dependent on certain physical characteristics. Dudley[26] noted that mature men of dark complexion and stocky build had less tendency to develop the symptoms of selenium poisoning than did younger men with smaller build and fair complexion. Wands[128] indicated that this effect might more reasonably be due to dietary habits of ethnic or nationality groups, such as the high level of wheat protein in Italian diets.

Besides the more obvious irritation effects of selenium and its compounds, it appears that some toxic action results from the blocking of several enzyme systems.[13,106]

2.1.2 Acute Poisoning

The intense irritation produced by dusts and fumes of selenium and its compounds normally prevents excessive exposure to high concentrations of selenium, and hence acute poisoning is uncommon. Moxon and Rhian[84] noted that the early signs of acute poisoning are nervousness and fever, followed by vomiting, then quietness and somnolence. Difficult breathing develops, followed by opisthotonos (tetanic spasm), clonic spasm, and falling blood pressure. Death may occur from respiratory failure, or convulsions resulting from action on the nervous system.

2.1.3 Retention and Elimination

Studies of Glover[44] and others[12,19] indicate that there are no apparent long-term systemic effects in humans as a result of chronic exposures to selenium and its compounds. Thus the body must have mechanisms for the effective removal of selenium so that accumulation of toxic amounts do not occur. Animal experiments suggest that, at least at low concentrations, the urinary and fecal excretion rates attain a steady state during long periods of exposure to selenium. Results of studies by Smith et al.[112] indicate that cats administered daily oral doses of selenite (equivalent to 20 and 100 μg of selenium per kilogram of body weight) excreted approximately 75 percent of the selenium in the urine and feces. When a toxic dose rate (equivalent to 250 μg/kg of selenium) was administered, the average excretion dropped to approximately 64 percent of the total intake.

The selenium not accounted for in the urine and fecal excretion may be (1) retained in the body, (2) excreted as a volatile compound in the breath and sweat, or (3) deposited in the hair. The importance of the first possibility depends on the amounts excreted by the latter routes. No experimental data are available for direct comparison of the contribution of each of the possible excretion routes. However, some data indicate

that excretion of volatile selenium compounds in the breath and sweat is a significant excretion route. Schultz and Lewis[99] found that when sodium selenate was administered subcutaneously to cats as sodium selenite in a dose equivalent to 2,500 to 3,500 μg of selenium per kilogram of body weight, 17 to 52 percent of the selenium was eliminated as a volatile compound within 8 hours. In a similar experiment McConnell[72] found that 3 to 10 percent of the initial subcutaneously administered selenite (equivalent to 3,000 to 4,000 μg of selenium per kilogram of body weight) was exhaled in 24 hours—half, moreover, in the first 3 hours. Selenium is also deposited in the hair in amounts dependent on the selenium concentration and duration of the exposure.[89]

According to Cerwenka and Cooper,[12] "Animal experiments indicate that as soon as a certain state of saturation is reached, the excretion holds pace with the intake." If correct, this means that the maximum amount of selenium retained in the body is dependent upon the level of exposure and not the duration of the exposure. This may not be true of ingested organic selenium compounds.[113]

The selenium that is retained is widely distributed in the body. Ermakov[31] found that selenium was widely distributed in human organs and tissues, and that there was a significant

difference in the distribution pattern among individuals. Animals chronically exposed to toxic amounts of selenite are found to retain most of the selenium in the liver, kidney, spleen, pancreas, heart, and lungs.[39] Once removed from exposure to selenium, the animals rapidly eliminated almost all the selenium in the body, mainly in the urine[113] within about 2 weeks.[3,112] After this period elimination rapidly decreases to a very slow rate that continues for a month or longer. Ingested organic selenium appears to be retained in the body longer than the inorganic selenium compounds.[113]

2.1.4 Detoxification

In the human body natural detoxification occurs through reduction of selenium compounds to elemental selenium, which is apparently not toxic[19] and is excreted through the kidneys and liver.[53,108] Elemental selenium is also converted to a volatile compound,[53] probably dimethyl selenide,[99] which is eliminated through the breath and sweat.

There are several methods of artificial detoxification or prevention of selenium poisoning, at least for animals. Animal studies have shown that protein, particularly casein, can help prevent intoxication from small amounts of ingested selenium.[46,70,107] Thus a high protein diet may be an important factor in protecting humans against chronic selenium

poisoning. Several studies have shown that arsenic can counteract the toxicity of selenium in rats,[25,88] dogs,[94] and pigs.[125] Amor and Pringle[2] suggested the use of an arsenic tonic for protection of selenium workers, but it has never been tried. Bromobenzene has been used to accelerate the excretion of selenium in the urine.[97] However, some investigators[4] found that this compound, administered orally, produced no effect on the selenium content of the body.

2.1.5 Selenium in Nutrition

Preliminary findings indicate that selenium may be a beneficial element to humans.[101] In Jamaica the protein-deficiency disease kwashiorkor, which is characterized by an inability to gain weight, appears to respond favorably to a diet supplement of 25 μg of selenium as γ, γ'-diselenodivaleric acid. It has already been demonstrated that selenium is an essential dietary nutrient for animals.[100,135] Selenium is prescribed for such animal diseases as congenital white muscle disease, selenium-responsive unthriftiness in cattle, exudative diathesis in poultry, and hepatosis diaetetica in pigs, as well as for barrenness in ewes.

2.1.6 Elemental Selenium

Studies to date indicate that elemental selenium is relatively nontoxic. However, dust or fumes of selenium cause

irritation of mucous membranes when inhaled. The selenium particulates are collected in the upper nasal passages and cause catarrh, nosebleed, and loss of the sense of smell.[2] Dermatitis can also occur when sufficient amounts come in contact with the skin.[2]

A detailed description of an industrial exposure to red selenium fumes is related by Clinton.[16] Exposure to the fumes, which have an unpleasant, sour, garlic-like odor, resulted in immediate and intense irritation of the eyes, nose, and throat. Heavily exposed workers noted a severe burning sensation of the nostrils, immediate sneezing, coughing, nasal congestion, dizziness, and redness of the eyes. Two to four hours after the exposure, severe headaches, mainly in the frontal region, were experienced, and lasted until the following day. The most heavily exposed workers had edema of the uvula and slight difficulty in breathing, while more pronounced dyspnea was noted in one case. No selenium could be found in the urine, and after 3 days all workers were entirely well and suffered no persistent aftereffects.

2.1.7 Selenium Dioxide, Selenites, Selenates

Selenium dioxide (SeO_2) and selenite salts (SeO_3^{-2}) readily form selenious acid in the presence of moisture. Selenious acid and its precursors are among the more toxic and

irritating compounds of selenium. Exposure to selenium dioxide has been reported to cause severe dermatitis[92] and burning of the eyes, with intense pain, lacrimation, and congestion of the conjunctiva.[76] Glover[43] noted that some people, particularly fair-haired workers, appear to become allergic to selenium dioxide; thus, on walking into a room where selenium dioxide is present their eyes will puff up, while others in the room exhibit no ill effect.

In general, susceptibility to the toxicity of selenium compounds varies widely from one individual to another.

2.1.8 Hydrogen Selenide

Hydrogen selenide (H_2Se) at room temperature is a gas with a very offensive odor.[19] This selenide, probably the most toxic and irritating of selenium derivatives, can be formed by the reaction of selenium with organic matter or certain other elements, as well as from selenides by acids or in some cases by water.

The symptoms of hydrogen selenide poisoning include nausea, vomiting, metallic taste, garlic odor of the breath, dizziness, extreme lassitude, and fatigability.[2,8,28] These symptoms were observed in one case from exposure to 800 $\mu g/m^3$ (0.2 ppm) of hydrogen selenide for less than 1 month. The symptoms of acute hydrogen selenide poisoning were described by Symanski[115]

as acute irritation of the mucous membrane of the respiratory tract, pulmonary edema, severe bronchitis, and bronchial pneumonia.

Dudley and Miller[29] noted that a person rapidly loses his ability to detect the odor of hydrogen selenide because of olfactory fatigue. These authors also mention that 5,000 $\mu g/m^3$ of this substance was intolerable to man and caused ocular and nasal irritation.

2.1.9 Selenium Oxychloride

Selenium oxychloride is a liquid which is used as a solvent for paints and varnishes, as a chlorinating agent, and as a resin plasticizer. Although it is strongly vesicant[27] and the vapors toxic, the danger of poisoning is not as great as might be supposed since the oxychloride has a low vapor pressure and readily decomposes in air.

2.1.10 Organoselenium Compounds

There is a very limited amount of data on the organic selenium compounds.

Motley et al.[81] reported acute sore throats in three laboratory workers following exposure to dimethyl selenide or combined organoselenium from handling dogs injected with selenium. One worker contracted pneumonitis.

2.2 Effects on Animals

Most reported cases of animal poisoning result from the ingestion of plants or foods containing toxic amounts of selenium, usually bound with organic compounds. Cases involving cattle, sheep, horses, and hogs have been described.[97] Numerous animal experiments involving selenium and its compounds have been reported. The results of some of the experiments have already been discussed in the sections concerned with Effects on Humans. Selenium from different sources produces different clinical and pathological symptoms in animals because of the various selenium compounds present in the sources. For example, Rosenfeld and Beath[97] give the following order of toxicity from equivalent amounts of selenium from different sources: wheat > corn > barley > selenite > selenate. However, in animals, subacute poisoning from selenium in general produces pneumonia, fatty degeneration of the liver, and degeneration of kidney cells and these symptoms clear up without residual pathology when exposure is discontinued. There is also evidence suggesting that selenium may cause cancer of the liver in rats.

Studies have shown that selenium is a necessary dietary element for many animals, including mammals and birds.[97]

2.2.1 Livestock

Acute poisoning of livestock occurs from the consumption

of highly seleniferous weeds—usually in a single feeding—in many cases resulting in death in a few hours. When the acute poisoning begins to take effect, the movement and posture of the animal become abnormal.[4] Diarrhea usually follows, the temperature rises, and the pulse becomes rapid and weak. Respiration becomes labored, with mucous rales and possible blood froth from the air passages. Bloating is usually pronounced, accompanied by abdominal pain, and urine excretion increases greatly. Pupils dilate. Complete prostration and apparent lethargy occur just before death from respiratory failure. Emesis, diarrhea, apathy, and paresis have been noted in pigs suffering from selenium poisoning.[86]

Chronic poisoning can be divided into three types, depending on the source of selenium: (1) blind staggers, caused by organic selenium compounds (with or without small amounts of selenate), which can be readily extracted with water from native selenium-bearing plants; (2) alkali disease, produced from consumption of plants or grains containing protein-bound selenium which is insoluble in water; and (3) chronic selenium poisoning, produced experimentally from pure inorganic selenium compounds. A summary of the three diseases is given in Table 1, which has been compiled from the studies cited by Rosenfeld and Beath.[97] (See paragraphs under Section 2.3 for a discussion of plants containing selenium.)

TABLE 1

SYMPTOMS AND GROSS PATHOLOGY OF CHRONIC SELENIUM POISONING IN LIVESTOCK[97]

	Blind Staggers	Alkali Disease	Experimental Selenosis
Selenium source	Certain selenium "indicator" plants	Seleniferous grains and grasses	Selenite and selenate inorganic salts
Symptoms	1st stage: increased desire to eat, animal staggers 2nd stage: increased loss of muscular control, front legs become very weak, does not eat or drink 3rd stage: paralysis, nearly blind, abdominal pain, body temperature drops, emaciation, eyes swollen and inflamed, cornea cloudy, death usually occurs in 3rd stage	Lameness, loss of vitality, elongated and hardened hoofs, loss of hair from mane and tail, anemia, stiffness of joints, roughened coat	Emaciation, some loss of muscle control, trembling of skeletal muscles, anorexia
Gross pathology	Necrosis (with cirrhosis) of liver, nephritis (subacute and chronic), enlarged gall bladder, soft and flabby heart, impacted intestinal tract with irritation	Atrophy and cirrhosis of liver; chronic nephritis; soft, flabby, and atrophied heart; edema of lungs	Necrosis with occasional cirrhosis of liver, acute nephritis, ulceration and gangrene of intestinal tract

2.2.2 Experimental Animals

Selenium poisoning in animals from administration of selenium and its compounds may be acute, subacute, or chronic, depending on the compound, dose, and duration of the exposure.

Acute symptoms in animals are garlicky odor, nervousness, fear, vomiting, and diarrhea.[97] This is followed by quietness and somnolence, difficult respiration, and decreased reflexes. Opisthotonos (tetanic spasm in muscles) follows. The blood pressure continually drops until death results from respiration failure.

In rats, subacute and chronic selenosis produce loss in body weight and anorexia, followed by cachexia, while ascites edema may also develop.[97]

Smith et al.[110] noted that among the common laboratory animals the cat showed the greatest susceptibility and the rat the greatest resistance to selenium poisoning.

2.2.2.1 Selenium, Selenites, Selenates

Hall et al.[50] exposed cats, guinea pigs, and rabbits to elemental selenium dust (which may have been contaminated with selenium dioxide) at the concentration of 30,000 $\mu g/m^3$ for 16 hours. This exposure produced mild interstitial pneumonitis in the animals. Selenium fumes via vacuum evaporation cause acute toxic reactions in rats.

The susceptibility of animals to the toxicity of sodium selenite and selenate has been studied by Franke and Moxon,[39,40] Heinrich and MacCanon,[60] and Painter.[87] Sodium selenite appears to be more toxic to rats than sodium selenate by a factor of 1.5 to 1.6. A comparison of the toxicity of selenium compounds with that for compounds of tellurium, arsenic, molybdenum, and vanadium is given in Table 2.

2.2.2.2 Hydrogen Selenide

Dudley and Miller[28,29] investigated the effect of inhalation of hydrogen selenide (H_2Se) on guinea pigs. All guinea pigs exposed to H_2Se in the concentration of 20,000 $\mu g/m^3$ for 60 minutes died within 25 days; 93 percent of the guinea pigs inhaling 43,000 $\mu g/m^3$ for 30 minutes died within 30 days; and after 570,000 $\mu g/m^3$ for only 10 minutes, all guinea pigs died within 5 days.[28] Additional studies were conducted on guinea pigs with various concentrations ranging from 1,000 to 45,000 $\mu g/m^3$ of H_2Se and for periods of 2, 4, and 8 hours. Table 6 in the Appendix summarizes the reported data. The major cause of the deaths seemed to be pneumonitis caused by irritation of the respiratory tract. In addition, damage to the liver and spleen was observed. At concentrations of 7,000 $\mu g/m^3$ and less no response was observable in the guinea pigs during the exposure periods. In one experiment (8 hours at 42,000 $\mu g/m^3$) it

TABLE 2

MINIMUM DOSES FATAL TO RATS OF COMPOUNDS OF SELENIUM, TELLURIUM, ARSENIC, VANADIUM, AND MOLYBDENUM[39]

Compound	MFD 75/48 hr*
Sodium selenite (Na_2SeO_3)	3,250 - 3,500
Sodium selenate (Na_2SeO_4)	5,250 - 5,750
Sodium tellurite (Na_2TeO_3)	2,250 - 2,500
Sodium tellurate (Na_2TeO_4)	20,000 -30,000
Sodium arsenite (Na_2HAsO_3)	4,250 - 4,750
Sodium arsenate (Na_2HAsO_4)	14,000 -18,000
Sodium vanadate ($NaVO_3$)	4,000 - 5,000
Ammonium molybdate ($(NH_4)_6Mo_7O_{24}$)	>160,000

*Minimum fatal dose to at least 75 percent of the rats in 48 hours (in micrograms of compound per kilogram of weight) via intraperitoneal injection.

was noted that the guinea pigs spread selenium-containing exudate over their bodies which caused irritation of eyes and nose.

2.2.2.3 Organoselenium Compounds

Moxon and co-workers[82,83] found that in general the organic compounds are retained by the tissues to a greater extent, and for a longer period of time, than are the inorganic compounds. However, there is a wide variation in the toxicity of different organoselenium compounds. The lethal doses for some organic compounds for rats via intraperitoneal injection are: for selenocystine, the equivalent of 4,000 µg of selenium per kilogram of body weight; for n-propylseleninic acid, 20,000 to 25,000 µg selenium; for B-selenodipropionic acid and for B, B - diselenodipropionic acid, 25,000 to 30,000 µg selenium.[82,83]

Animal experiments with dimethyl selenide indicate that this compound has a low degree of toxicity in mice and rats[74] when injected intraperitoneally.

2.2.3 Carcinogenesis

There are data which indicate that selenium may be carcinogenic to animals, and therefore possibly to man. However, further investigations are needed to clarify the point. In studies made by Nelson et al.[85] and Fitzhugh et al.,[38] 126 rats were fed selenium in organic combination with corn and wheat (containing 5 to 10 ppm selenium) and also inorganic selenides

(10 to 50 ppm). Of the 53 rats that lived over 18 months, 11 developed hepatic neoplasms of low malignancy, and four developed microscopic adenomatoid hyperplasias. None of the neoplasms metastatized. Rats that died before 18 months did not exhibit necplasms. On the basis of these early tests, the Food Additive Amendment of 1958 included selenium in the cancer clause.[41] Concern for the carcinogenic hazard of selenium in foods was also shown by the National Academy of Sciences[93] and the World Health Organization.[32]

However, it was thought by some people that the data were insufficient to prove the carcinogenic hazards of selenium, and they urged a careful reevaluation of the problem. Some suggested that the diet in the experiments of Nelson et al.[85] was inadequate in protein. Pearce[90] failed to induce cancer in rats by sodium selenite feeding, but the experiment was terminated before 18 months, the time that the Nelson experiments began producing "cancer." Clayton and Baumann[15] found that 5 ppm of sodium selenate appeared to decrease the susceptibility to azo-dye-induced cancer of the liver. Furthermore, although the hepatotoxicity of excess selenium is well known, no report of liver cancer resulting from chronic selenium poisoning in farm animals has been found in the literature.

Frost[42] cited the work of Tsuzuki et al.,[123] who studied rabbits and mice under conditions simulating industrial exposure to selenium vapor and exposure to selenium metal dust. The authors reported that tumors formed in the subcutaneous tissue of the dorsal neck in some of the mice after unusual exposures to selenium. The tumors were considered to be adenomas, similar histologically to cylindromas. The tumors apparently did not metastasize.

Tscherkes and co-workers[121,122,124] studied rats fed mixtures of sodium selenate (430 and 860 µg Se/100,000 µg of diet) and casein (12 to 30 percent). To some mixtures other ingredients were added, including riboflavin, cystine, chlorine, and nicotinic acid. The overall tumor incidence was 8.5 percent of the 200 rats. Four rats developed hepatoma neoplasms, two of which had pulmonary metastasis. Sarcomas were found in seven rats, one sarcoma in the liver and the others in the mesenteric lymph nodes. There were four rats with adenomas and the same number with precancerous tumor forms.

Harr et al.[57] also studied rats fed selenites and selenates (from 0.5 to 16.0 ppm Se) with 12 or 22 percent casein added. No neoplasms were found that could be attributed to the selenium in the diet. However, three types of lesions were found: (1) acute toxic hepatitis associated with osteodystrophy,

icterus, and fluid imbalance; (2) chronic toxic hepatitis associated with chronic passive congestion, reticulosis, myocarditis, productive pancreatic duct hyperplasia, hepatocyte hyperplasia, and hepatic necrosis; and (3) hepatic hyperplasia associated with abnormal hepatic foci.

2.3 Effects on Plants

No studies were found concerning the effects of atmospheric selenium on plants. However, it has been well established that certain types of plants require selenium to grow, that they can accumulate high concentrations of selenium from seleniferous soils, and that some will even emit volatile selenium compounds into the air. Furthermore, while some plants can store up very high concentrations of selenium (up to 10,000 ppm), others (e.g., corn and wheat) can be damaged by the accumulation of small amounts (300 ppm). Kubota et al.[65] summarized their work and others on the selenium content of plants in the United States. Figure 1 shows the average selenium content of plants for 480 counties in 46 of the States.

2.3.1 Selenium Indicator Plants

Plants that can grow only in soil containing selenium and can accumulate large amounts of selenium are referred to as "Beath's selenium indicators."[5,97] A number of these plants' blossoms emit an offensive, garlic-like odor caused by the

+ Counties in which greater than one-half of the plants contained less than 0.1 p.p.m.
• Counties in which greater than one-half of the plants contained more than 0.1 p.p.m.
· Counties were more than 50 p.p.m. of selenium was found in selenium-accumulator plants but no data available in selenium content of forages or grains.

FIGURE 1

Selenium Content of Plants in Certain Counties in the United States[65]

production of volatile selenium compounds. To an experienced person the intensity of the odor provides an indication as to the amount of selenium in the plant, which is related to the amount in the soil.

These "primary" indicators normally grow in the soil of arid and semiarid regions and are generally found in the Midwestern and Western parts of the United States. Included in the list of indicator plants are 24 species and varieties of Astragalus (milk vetch, with pea-like flowers), section Xylorhiza (woody aster) of Machaeranthera, section Oonopsis (goldenweed) of Haplopappus, and Stanleya (princes plume). The geographical distribution of these plants is shown in Figure 2.

These plants contain large amounts of selenium, generally 1,000 to 10,000 ppm. The consumption of these plants by livestock produces the disease syndrome of blind staggers or acute selenium poisoning discussed in Section 2.2.1.

2.3.2 Secondary Selenium Absorbers

Other types of plants also accumulate substantial amounts of selenium (generally 50 to 500 ppm), but less than the "indicator plants." However, they do not require selenium in the soil for growth. These secondary selenium absorbers include species of Aster, Atriplex, Castilleja, Camandra, Grayia, Grendelia, Gutierrezia, Machaeranthera, and Mentzella. They can be

FIGURE 2

Distribution of Seleniferous Vegetation[67]

used to indicate seleniferous soils through analysis of their selenium content.

These secondary absorbers can accumulate only water-soluble selenium from the soil. This is in contrast to the indicator plants which can accumulate selenium from the soil regardless of the form of selenium present. The secondary selenium absorbers may produce acute or chronic selenium poisoning when consumed by livestock.

2.3.3 Grains, Vegetables, Grasses, and Other Vegetation

Most grains, vegetables, and grasses could also be classified as secondary selenium absorbers in that they may similarly absorb and accumulate water-soluble selenium compounds from the soil. However, the maximum amount of selenium that is accumulated by these plants is generally less than 30 ppm.[97] Wheat, barley, corn, oats, and rye that have been grown in a seleniferous soil contain 0.1 to 30 ppm selenium.[134] Vegetables normally accumulate less than 1 ppm in selenium-containing soils, but values as high as 18 ppm have been noted.[134] The content of selenium in native grasses is quite variable. They sometimes contain as much as 84 ppm selenium.[97] Consumption of plants that contain high amounts of selenium usually produces alkali disease in livestock.

Crop plants are damaged by accumulation of large amounts of selenium (30 to 300 ppm). The most common symptom of selenium poisoning in plants is inhibition of growth. Some crops, particularly wheat, barley, and rye, will exhibit chlorosis. Younger plants are more susceptible, and their growth inhibition is greater than that of mature plants.

Hamilton and Beath[54,55,56] have recently studied a large number of plants for their uptake and distribution of various forms of selenium. These plants, including 20 range plants, 17 crop plants, and 18 vegetables, were studied while growing in an artificially selenized soil under greenhouse conditions. It was found that the distribution of selenium within a plant varied widely and that all the plants could accumulate toxic amounts of selenium.

Other vegetation, including tobacco, also can accumulate selenium. However, because these types of vegetation accumulate only small amounts of selenium and have not poisoned animals, they have not been as well studied. Dye et al.[30] determined the selenium content of some plants as follows:

Plant	Se Content ppm (avg.)
Pear leaves	0.45
Apple leaves	0.53
Radish leaves	0.28
Lettuce leaves	0.60
Corn	0.32
Wheat	0.29

2.4 Effects on Materials

There is no information at present indicating that atmospheric selenium would have any detrimental effect on materials.

2.5 Environmental Air Standards

The American Conference of Governmental Industrial Hygienists (ACGIH) has set the threshold limit values for occupational exposure during 40-hour weeks with 8-hour days at 200 $\mu g/m^3$ for selenium compounds, except in 1967 when the limit for selenium hexafluoride was set at 400 $\mu g/m^3$.[118] In 1962, the value was lower, 100 $\mu g/m^3$ for selenium compounds.[24]

No country has yet established a 24-hour threshold limit value.

3. SOURCES

3.1 Natural Occurrence

Selenium is widely distributed in the earth's crust at a concentration of about 0.09 ppm.[45] However, it is mainly concentrated in sulfide minerals and in the soil of the dry plains of the Midwestern United States. Furthermore, some plants can absorb and accumulate selenium in large amounts from the soil. (See Section 2.3 for a discussion of these plants.)

Despite its wide distribution in nature, selenium is not an essential constituent of any common rock-forming mineral. However, it is recognized as a major constituent in at least 22 selenides, 6 sulfosalts, 1 oxide, 4 selenites, and 1 selenate, and as a minor constituent of 24 sulfides and tellurides, 5 sulfosalts, and 1 tellurite. The important selenium minerals are berzelionite (Cu_2Se), tiemannite (HgSe), and naumannite (Ag_2Se).[20] Selenium is associated mainly with copper, iron, lead, silver, gold, and uranium, and is often found with pyrite, chalcopyrite, bornite, and other sulfide minerals.[79] Weathering releases much of the selenium from these minerals; it may remain as native selenium or, more often, be redeposited as ferric selenite in secondary iron minerals such as limonite. Luttrell[71] has prepared a partial list of selenium-bearing minerals.

Selenium can be found in coal (see Section 3.4), igneous rocks, hydrothermal deposits, and sedimentary rocks.[67] In igneous rocks and in sulfide ores probably most of the selenium is widely distributed as selenides. Volcanic rocks in various parts of the Western United States contain as much as 120 ppm selenium,[22,34] and still higher concentrations are present in some volcanic sulfur deposits.[10] Hydrothermal ore deposits containing high concentrations of selenium are widespread. Some of the more common are those associated with epithermal gold and silver deposits, as well as with antimony and mercury epithermal deposits.[67] Large amounts of selenium in small concentrations are found in copper deposits of the porphyry type and in massive sulfide deposits, such as those in the Southern Appalachians.

Several studies have been made of sedimentary rock formations (particularly in the Western United States[67]), many of which support poisonous seleniferous vegetation. Beath et al.[6] found that sandstone from the Poison Butte area of Wyoming contains 112 ppm selenium, that carbonaceous siltstone in western Wyoming contains 680 ppm, and that phosphate rock contains as much as 212 ppm selenium. The Pierre Shale of the Western United States, a carbonate rock, contains as much as 26 ppm selenium.[10] Carbonate rock from the Phosphoria Formation in

Idaho, Montana, Utah, and Wyoming contains selenium ranging from 1 to 100 ppm, with an average of 19 ppm.[67]

Highly concentrated deposits of selenium have also been found in the volcanic tuff of the Wind River formation of Wyoming,[34,120] and in sandstone-type uranium deposits, particularly in the Gas Hills area of Wyoming and the Ambrosia Lake district of New Mexico.[67]

Selenium cannot be mined profitably, with the present methods of technology, because of the low concentration of selenium in mineral deposits. Therefore, selenium must be derived as a by-product in the refining of other ores.

3.2 Production Sources

Quantities of selenium in mineral deposits are not sufficient to make its extraction alone profitable. It therefore is obtained as a by-product from other processes.

The principal source of selenium is as a by-product from the copper refineries; smaller amounts are obtained from lead smelters and from the selenium-containing sulfur residues from the chemical industry.[67] Other sources are the refining of various sulfide ores (gold, silver, nickel) and uranium ores, as well as the making of paper (when pyrites are used as the source of sulfur in the manufacturing process).

In the smelting of copper ores, part of the selenium remains with the crude or blister copper (about 0.05 percent selenium), and part is carried through the flues as fumes and dust which are collected and returned to the reverberatory furnaces.[20] Dust from the lead smelters is also added to this circulating stream of flue gases. In the electropurification of the copper, the selenium precipitates with other metallic products in the mud or slime that collects beneath the anode. This anode mud, ranging from about 0.05 to 10 percent selenium, is usually refined by one of the following fundamental processes: smelting with soda ash, roasting with soda ash, and roasting with sulfuric acid to yield about 98 to 99 percent pure selenium metal, with arsenic as the major impurity.[77]

High-purity selenium, used in electronics, is made by several methods such as fractional distillation, zone refining, and catalytic oxidation to selenium dioxide followed by either gaseous or wet reduction.[77]

The United States is the major producer and consumer of selenium. In 1967, six companies in the United States produced selenium.[9] They are listed in Table 7 in the Appendix. Of these, the Kawecki Chemical Company is a metal and alloy manufacturing company. The remaining companies produce selenium as a by-product in the copper refining process. Table 8 in

the Appendix summarizes the production, apparent consumption, and price of selenium for 1956 through 1967 in the United States.

3.3 Product Sources

Selenium has a variety of applications, but most require only small quantities of the metal. The major users are the electronic and electrical industries, in which 90 percent of the selenium is used in the manufacture of dry plate rectifiers, while the rest is used mostly in photoelectric cells.[20] The chemical industry is the next largest user, accounting for over one-third of the total consumption. The glass industry and xerography manufacturing also use significant amounts.

The major uses of selenium and its compounds are as follows:

Rectifiers: These are used extensively in electroplating, welding, direct-current motor operation, and induction braking, and in battery chargers, magnetic coils, arc lamps, and voltage regulators. About 0.5 to 25 g of selenium are used per rectifier, depending on cell size.

Photoelectric cells: These cells, which require about the same amount of selenium as rectifiers, are used in photographic exposure meters, detectors, electric eyes, colorimeters, and pyrometers.

Pigments: The largest use of selenium by chemical industries

is for pigments. Selenium is compounded with cadmium sulfide to prepare the orange, red, and maroon cadmium sulfoselenide pigments used to color plastics, paints, enamels, inks, and rubber.

Glass: Selenium, sodium selenate, barium selenite, and sodium selenite are added (0.02 to 0.3 lb/ton of glass) to neutralize green tint from iron impurities in glass. A slightly larger amount is added to produce a pink tinge for such products as milk bottles and other food containers. Ruby-red glass (used in tableware, vehicular taillights, traffic and signal lights, light filters, and infrared equipment) requires about 1 to 50 pounds of selenium per ton of glass. Selenides of the arsenic groups are used to make low-melting-temperature glasses, primarily for research purposes.

Lubricants: Tungsten diselenide (WSe_2) and columbium diselenide ($CbSe_2$) powders are used as solid lubricants directly applied to rubbing surfaces or mixed with other greases and with various metals, ceramics, and plastics to form self-lubricating parts. Applications include the vacuum, radiation, aerospace, electromechanical, and instrumentation fields.

Blasting caps: Selenium, with barium peroxide and tellurium, is used for variable, delayed-action, gasless fuse powder in blasting caps. Almost 10,000 pounds of selenium and tellurium mixture are used annually in this capacity.

Chromium plating: Selenate solutions, ranging from 0.012 to 0.020 g/liter, are used in chromium-plating solutions which impart a superior corrosion-resistant property and a dull luster (for prevention of glare) to the plated material.

Stainless steel: Selenium improves the casting, forging, and machinability of stainless steel without reducing its corrosion resistance or hot-forging and cold-working properties. Selenium content varies from 0.01 to 0.35 percent.

Medicines: In the form of sodium selenate solution, selenium is used to control certain animal diseases[49] such as congenital white muscle disease in sheep, selenium-responsive unthriftiness in cattle, exudative diathesis in poultry, and hepatosis diaetetica in pigs. This solution is also used to overcome sterility in ewes.

Photocopiers: Amorphorus selenium is used in the xerography process.

There are many minor uses of selenium and its compounds, such as: in preparation of pharmaceuticals (e.g., niacin and cortisone); in deodorants; as accelerating and vulcanizing agent in rubber products; as catalysts for oxidizing, dehydrogenating, and hardening of fats used in soaps, waxes, edible fats, and plastics; in printing inks, transformer oils, mineral oils, and vegetable oils as an antioxidant; in linseed, oiticica,

and tung oils for nondrying properties; in insecticides, parasiticides, bactericides, and herbicides; in photographic photosensitizers and toners; in mercury vapor detectors; as fireproofing agents for textiles and wire cable coverings; as insect repellants; as phosphorescents and luminescents. Selenium oxychloride is a powerful solvent used as a paint and varnish remover and for rubber resins, glue, and other organic substances.

Applications which appear to be increasing are xerography copying; steel production; preparation of red color television phosphor (ZnSe), electrolytic manganese, and colored anodized aluminum; and use in solid lubricants. There are new applications of selenium in animal health and nutrition.[9]

No recent figures could be found providing a breakdown by uses of the consumption of selenium and its compounds; however, Minerals Yearbook[80] includes a breakdown of the consumption for 1955. A list of merchandisers and consumers of selenium and its compounds is given in Table 9 in the Appendix, while Table 10 in the Appendix lists some selenium compounds and their uses, and Appendix Table 8 includes consumption and price statistics.

3.4 Other Sources

Selenium air pollution may occur from the heating or burning of materials that contain selenium. Thus incineration

of manufactured selenium products (see Section 3.3) may be a pollution source if not properly controlled. In addition, the burning of coal and other natural materials that contain sulfur can also be a source of selenium pollution. Normally where sulfur is found, selenium can also be found. Materials from terrestial sources such as fuels and ores generally have a selenium-to-sulfur ratio of approximately 1×10^{-4}.[59]

Little information is available on the selenium content of the various materials and products that are incinerated every day. Some possible sources of selenium include natural fuels, leather goods, cloth materials, wood products, etc. West[130] has found selenium in paper products including cigarette paper, newspaper, etc. (see Section 3.5). Lakin and Davidson[66] summarized the data on the selenium content of different coals. As can be seen from Table 3, the selenium content has been found as high as 7.38 ppm selenium in lignite coal.

TABLE 3

SELENIUM CONTENT OF COALS[66]

Sample Location	Type of Coal	No. of Samples	Selenium Content (ppm) Range	Average
Western Wyoming	Lignite	3	1.96-7.38	3.88
Montezuma County, Colo.	"	2	2.0 -2.4	2.2
Sandoval County, N. Mex.		1		0.1
Morley, Alberta, Canada		1		2.0

3.5 Environmental Air Concentrations

Only one published report was found relating to the atmospheric concentration of selenium in the United States. Hashimoto and Winchester[59] in 1964-1965 measured the selenium content in samples of rain, snow, and air collected on the campus of the Massachusetts Institute of Technology (Cambridge, Mass.), in the semirural areas of Topsfield and Boxford, Mass., and in the smaller city of New Haven, Conn. The data are shown in Table 4. In Cambridge, the average selenium concentration was 0.21 μg per liter of precipitation, which on the basis of air samples is approximately equivalent to 0.001 $\mu g/m^3$ of air or 1 nanogram per cubic meter. Air samples (100 m^3) were taken by passing air (1 m^3/hr) either through an aqueous bubbler or through a 1-micron pore diameter Millipore filter.

TABLE 4

ATMOSPHERIC SELENIUM (1964-65)[59]

Location[a]	Date 1964-65	Se in μg[b]	Remarks
1	Dec. 18	0.15	Falling snow
2	Dec. 18	0.09	Falling snow
1	Jan. 3	1.40[c]	Rain + ice
2	Jan. 3	0.70	Rain + ice
1	Jan. 10	0.13	Falling snow
2	Jan. 10	0.16	Falling snow
1	Jan. 16	0.53	Falling snow
2	Jan. 16	0.52	Falling snow
1	Jan. 24	0.14	Falling snow
2	Jan. 24	0.16	Falling snow
3	Feb. 22	0.25	Falling snow
2	Feb. 25	0.10	Rain
3	Mar. 20	0.08	Ground snow
2	Mar. 20	0.06	Falling snow
3	Mar. 29	0.10	Ground snow
1	Mar. 29	0.09	Falling snow
2	Mar. 29	0.10	Falling snow
Mean		0.21	
4	Jan. 31	0.08	Ground snow
5	Feb. 27	0.03	Ground snow
5	Mar. 20	0.12	Ground snow
6	Mar. 20	0.04	Ground snow
6	Mar. 20	0.10	Ground snow
1		0.11	Tap water
5	Feb. 27	0.09	Well water
1	May 11	0.03	Air, bubbler
1	May 20	0.03	Air, bubbler
1	May 20	0.11	Air, filter
1	May 27	0.13	Air, bubbler
1	May 27	0.16	Air, filter
1	June 1	0.06	Air, bubbler
1	June 1	0.10	Air, filter

[a]Sampling locations: 1. MIT campus, roof of earth science building. 2. Ground location near 1. 3. Cambridge, near Central Square. 4. Topsfield, Mass. 5. Boxford, Mass. 6. New Haven, Conn., Yale University campus.

[b]Micrograms of selenium per liter of water or 100 m^3 of air. One liter of water is roughly equivalent to 200 m^3 of air.

[c]Excluded from mean.

The rain or snow melt water (1 liter) was collected on polyethylene, filtered on filter paper to remove particulates, acidified, evaporated to a final volume of 0.1 ml, and analyzed by neutron activation. The bubbler solutions were processed similarly, while the Millipore filters were irradiated directly.

Based on the selenium-to-sulfur ratio (1×10^{-4}), which is similar to that found for geochemical materials, these authors concluded that the source of the selenium was probably from terrestrial sources, including fuels and ores used by industry. The authors also suggested that a study of the selenium-to-sulfur ratio in different locations may give some information about the length of time the selenium has been in the air and the sources of pollution.

Some unpublished results on the selenium content of particulates for various cities in the United States is given in Table 5.[117] The particulate matter was collected from ambient air. The analytic procedure involved extraction of the samples with hydrochloric acid and analysis of the extract by atomic absorption spectrophotometry.

A study is presently being conducted by Dr. Philip W. West[130] to determine the selenium content of air in Baton Rouge, La., and possibly in other areas. The preliminary investigation shows that there is a detectable amount of selenium in Baton

TABLE 5

SELENIUM CONTENT OF PARTICULATES IN AMBIENT AIR, 1965[117]

Location	Selenium Content ($\mu g/m^3$)*
California (Los Angeles)	<0.06
Colorado (Denver)	<0.05
Arizona (Phoenix)	<0.04
California (Long Beach and San Francisco)	"
Connecticut (Norwich)	"
Delaware (Newark and Wilmington)	"
District of Columbia	"
Hawaii (Honolulu)	"
Illinois (Chicago and East St. Louis)	"
Indiana (Dunes State Park, East Chicago, Indianapolis, Ogden Dunes)	"
Kentucky (Lexington)	"
Louisiana (New Orleans)	"
Maine (Portland)	"
Massachusetts (Lawrence)	"
Michigan (Grand Rapids)	"
Minnesota (St. Paul)	"
Missouri (St. Louis)	"
Montana (Helena)	"
Nevada (Las Vegas)	"
New Jersey (Glassboro, Marlton, Pemberton, Trenton)	"

*Values given are averages of 1965 quarterly composite of 5 to 7 samples; an air volume of 2,000 m^3 (25°C) is assumed.

Rouge, and that the probable source is trash burning. It was found that paper and other products of vegetation had a high concentration of selenium; for example, newsprint was found to contain up to 6 ppm selenium. The selenium content was thought to be a result of the accumulation of selenium in the initial tree or plant. However, Cole[17] thought that selenium could be introduced into paper from the pulping chemicals (e.g., the use of pyrites for the source of sulfur).

Lakin and Davidson[66] reported the results of analysis of particulate matter for selenium in 1941. The samples were collected from air-conditioner filters in various locations, as shown in Table 11 in the Appendix. The selenium content ranged from 0.05 to 10 ppm.

4. ABATEMENT

No study has been made of the methods for control of selenium and its compounds. However, based on the properties and on the methods of recovery and purification of selenium, wet scrubbers and high-voltage electrostatic precipitators should be effective. The common selenium atmospheric pollutants are probably selenium dioxide (or selenious acid in moist environments) and, to a lesser extent, hydrogen selenide. These compounds are all soluble in water, the former a solid and the latter a gas at ambient temperatures. Selenium metal, except for the red allotrope form, is insoluble in water. However, it is soluble in strong bases, forming selenium compounds, and it will burn in air, producing selenium dioxide.

In the recovery and purification processes of selenium,[67] wet scrubbers and electrostatic precipitators are used to collect selenium dioxide fumes given off during the smelting or roasting, as well as to collect red selenium. Furthermore, selenium emissions from trash burning are controlled by the use of wet scrubbers.[130]

At the present time, the chief industrial control methods are the use of a good ventilation system and personal protective equipment, including safety goggles and a respirator when working in a low airborne concentration, and a supplied-air

respirator in heavily contaminated areas.[102] Selenium-containing liquid wastes are disposed of by washing them down the drain, while solid wastes are buried.

5. ECONOMICS

No information has been found on the economic costs of selenium air pollution or on the costs of its abatement. Data on the production and consumption of selenium are presented in Section 3.

6. METHODS OF ANALYSIS

6.1 Sampling Methods

Air samples have been collected by means of electrostatic precipitators,[89] filters,[59] and liquid impingers.[59,63,89] All of these methods can be used for selenium dusts and fumes, while only the last can be used for collection of vapors or gaseous compounds.

The use of filters and liquid impingers are the most commonly used sampling methods today. Some air samples were taken by passing 100 m^3 of air at the rate of 1 m^3/hr through a 1-micron pore diameter Millipore filter. Because selenium is found in many filter papers, Millipore filters or other selenium-free collection media (e.g., glass fibers) should be used. However, some filter papers can be washed with sodium sulfide and water to remove traces of selenium. The liquid used in the impingers has been water[59,63] and a solution of 40 to 48 percent hydrobromic acid with 5 to 10 percent bromine. The water can be used with nonvolatile water-soluble compounds such as selenium dioxide.[89] The advantage of the hydrobromic acid-bromine solution is that it converts selenium and most of its compounds to the soluble selenium tetrabromide. This solution, after collection, can be analyzed directly after decolorization and neutralization,[63] or the selenium may be separated by distillation.

It has also been suggested that soda lime or silica gel could be used to collect vapors of selenium compounds.[89]

6.2 Qualitative Determination Methods

A quick qualitative estimation of selenium can be made by taking advantage of the reaction of aromatic 1,2-diamines with selenious acid (or Se(IV) cation) to form colored piaselenoles. Elemental selenium and selenides readily oxidize in nitric acid or hydrogen peroxide to selenious acid. Selenate salts—or Se(VI) cations—give only weak colors. The most common diamine employed is 3,3'-diaminobenzidine,[61] which forms a yellow dipiaselenole in acid and is sensitive to 10 ppm. The 4-dimethylamino and 4-methylthio derivatives of 1,2-phenylenediamine[98] will also react with selenious acid to give stable bright red and blue-purple colors, respectively. Reaction with 2,3-diaminonaphthalene has been used as a spot test.[35] Other ions—particularly copper, iron, tellurium, chromium, nickel, and cobalt—may cause interference in high concentration, but some may be masked by complexing agents such as EDTA. Other methods of detection of selenious acid that have been reported are reaction with (1) iodides,[91] (2) thiourea,[23] (3) diphenylhydrazine,[36] and (4) pyrrole,[114] as well as the catalytic effect on the reaction of methylene blue with alkali sulfide.[37]

6.3 Quantitative Determination Methods

Several quantitative methods of analyzing selenium are based on the reaction of selenious ion with 3,3'-diaminobenzidine. West and Cimerman[131] used this reagent in connection with the ring-oven technique. This colorimetric method is basically free from interferences when masking reagents are used; limit of identification is 0.08 µg, is applicable in the range of 0.1 to 0.5 µg.[129,131] Kawamura and Matsumoto[63] spectrophotometrically determined the selenium in air samples collected in impingers by measuring the absorbance of the solutions treated with this reagent. The benzidine reagent has also been used in fluorometric determination of selenium in biological materials.[14,21] Detection in these methods was in the order of 10 to 50 ppb selenium.

Walkinson,[126] as well as Allaway and Cary,[1] found that the product from 2,3-diaminonaphthalene and selenium showed a fluorescence sensitivity in the neighborhood of 0.5 to 5 ppb selenium--a sensitivity greater than that with the benzidine product.

Neutron activation methods have been used to determine selenium from air samples (via filters and aqueous bubbler) and from samples of snow and rain.[59] A sensitivity of 0.01 µg of selenium was obtained when gamma radiation was measured with a

scintillation spectrometer. This technique has also been used to determine traces of selenium in biological materials[7] and in metals.[18]

Recently West and Ramakrishna[132] have developed a method for determining trace amounts of selenium based on its catalytic effect in the reduction of methylene blue by sodium sulfite. Color comparisons are made in the range of 0.1 to 1.0 µg of selenium. There is serious interference from copper if present in an excess of 10 µg. Kawashima and Tanaka[64] also developed a catalytic method based on the reduction of 1,4,6,11-tetraazanaphthacene; this method is subject to interference from several ions.

Walkinson[127] has discussed some of the newer methods that are used in the analysis of selenium in biological material, including polarography, X-ray fluorescence, and atomic absorption spectrophotometry.

7. SUMMARY AND CONCLUSIONS

Selenium compounds, particularly the water-soluble compounds, are toxic to humans and animals. In humans, mild inhalation of selenium dusts, fumes, or vapors irritate the membranes of the eyes, nose, throat, and respiratory tract, causing lacrimation, sneezing, nasal congestion, coughing, etc. Prolonged exposure through inhalation can cause marked pallor, coated tongue, gastrointestinal disorders, nervousness, and a garlicky odor of breath and sweat. In animals, subacute selenium poisoning produces pneumonia and degeneration of the liver and kidneys. Furthermore, experiments with rats indicate that selenium may cause cancer of the liver.

The biochemical effects of elemental selenium and its compounds on humans is not as yet thoroughly understood. The selenium deficiency diseases found in animal species, as well as some of the frank selenium poisoning, have not been observed in man. Similarly, the carcinogenic hazard of selenium and the antagonistic effect of arsenic for selenium seen in animals are yet to be shown in humans. These are important factors that need clarification to properly evaluate the role of selenium and its compounds in air pollution.

There is no information indicating that atmospheric selenium has any detrimental effect on plants or materials. Some

plants contain large amounts of selenium that can be toxic to the plants themselves, as well as to humans and animals who ingest the plants.

Samples of snow, rain, and air taken in Boston, Mass., (1964-1965) show that the selenium content of the air is averaging 0.001 $\mu g/m^3$. Based on the selenium-to-sulfur ratio in these samples, the atmospheric selenium was probably from terrestrial sources, including the fuels and ores used by industry. Another source may be the burning of trash containing paper products. Some papers when analyzed contain as much as 6 ppm selenium. Selenium in paper may come from accumulation by the original tree or plant, or possibly from the manufacturing of the paper (from the use of pyrites in the process). Any vegetation which is burned may be a possible source of atmospheric selenium. Another source could be the refining of sulfide ores, particularly copper and lead ores.

Emissions of selenium and its compounds can be effectively controlled by use of electrostatic precipitators and water scrubbers.

No information has been found on the economic costs of selenium air pollution or on the costs of its abatement. Methods of analysis are available that can measure quantitatively in the parts per billion or submicrogram region. However none

of the methods is simple, rapid, or applicable to continuous monitoring, and many of the methods are not specific for selenium. A rough estimate as to the magnitude of selenium in the atmosphere might be made from the concentration of sulfur in the atmosphere. This method would be valid if the sources of these two pollutants are sulfide ores, fossil fuels, or igneous and sedimentary rocks, since in these materials the average weight ratio of selenium to sulfur is 1×10^{-4}.

Based on the material presented in this report, further studies are suggested in the following areas:

(1) Further determination of the atmospheric concentration of selenium compounds in the cities of the United States, particularly near copper refiners and other sulfide ore refiners, and near trash-burning sites.

(2) Determination of the long-term exposure effects on humans and animals, particularly in the concentration range found in the atmosphere.

(3) Determination of the amount of selenium in particulates.

(4) Investigation of the possibility of antagonistic, synergistic, or catalytic effect of selenium or its compounds with other substances in the environmental air.

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APPENDIX

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TABLE 6

MORTALITY OF GUINEA PIGS FROM INHALATION OF HYDROGEN SELENIDE [29]

Concentration ($\mu g/m^3$)*	Number of Guinea Pigs	Days 1-5	Days 6-10	Days 11-15	Days 16-20	Days 21-25	Days 26-30	% Dead Within 30 Days
2-hour exposure:								
6,000	16	0	0	1	1	0	0	12.5
12,000	16	3	2	2	1	0	0	50.0
13,000	16	1	6	0	2	1	0	62.5
21,000	16	4	2	5	2	1	0	87.5
34,000	16	5	0	3	3	0	0	68.8
36,000	16	11	3	0	1	0	0	93.7
4-hour exposure:								
6,000	16	1	2	0	0	0	0	18.8
7,000	16	2	0	1	1	0	0	25.0
12,000	16	2	6	3	1	0	0	75.0
15,000	16	8	5	1	1	1		100.0
45,000	16	15	1					100.0
8-hour exposure:								
1,000	16	0	2	4	0	1	1	50.0
1,000	16	1	3	1	1	0	2	50.0
1,000	16	0	7	2	0	0	0	56.3
6,000	16	15	3	2	2	1	0	81.3
6,000	16	7	3	0	3	1	0	87.5
7,000	16	5	2	5	1	1	0	87.5
42,000	16	14	2					100.0
Controls	32	1	1	0	1	0	0	9.4

*1 $\mu g/m^3$ = 0.000302 ppm.

APPENDIX

TABLE 7

PRODUCERS OF SELENIUM IN THE UNITED STATES (1967)[80]

Company	Location
American Metal Climax, Inc.	Carteret, N.J.
American Smelting and Refining Co.	Baltimore, Md.
International Smelting and Refining Co.	Perth Amboy, N.J.
Kawecki Chemical Co.	Boyertown, Pa.
Kennecott Copper Corp.	Magna, Utah
Kennecott Refining Corp.	Anne Arundel County, Md.

APPENDIX

TABLE 8

SALIENT SELENIUM STATISTICS, 1956-67[78,79,80]
(Thousands of pounds of contained selenium)

	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967
United States												
Producción[a]	928	1,077	727	799	620	1,022	999	928	929	540	620	598
Shipments to consumers	1,035	625	737	1,011	650	787	741	679	646	824	845	659
Imports for consumption	235	148	184	224	160	117	159	339	293	251	286	301
Consumption, apparent[b]	1,270	773	920	1,234	810	904	900	1,018	939	1,075	1,131	960
Producers' stocks, Dec. 31	191	651	551	339	290	515	773	1,022	1,305	1,021	797	736
Price per pound, commercial grade	$9.00-15.00	$7.50-12.00	$7.00-7.50	$7.00	$6.50-7.00	$5.75-6.25	$5.75-6.25	$4.50-5.75	$4.50-6.00	$4.50-6.00	$4.50-6.00	$4.50-6.00
World production	1,923	1,940	1,507	1,719	1,777	2,097	2,091	2,015	2,163	1,789	1,951	2,069

[a] Includes small quantity of secondary selenium for 1956-61.
[b] Total of shipment and imports to consumers.

APPENDIX

TABLE 9

LIST OF MERCHANDISERS AND CONSUMERS OF SELENIUM AND ITS COMPOUNDS[116]

Accurate Electronics Co.	Chicago, Ill.
Alliance Industrial Products Co.	Chicago, Ill.
Allied International Co.	New York, N.Y.
Allis-Chalmers Manufacturing Co.	Milwaukee, Wis.
Alloychem Inc.	New York, N.Y.
Alloys Unlimited Inc.	Long Island City, N.Y.
American Metal Climax Inc.	New York, N.Y.
American-Orient Products Corp.	Rochester, N.Y.
American Rectifier Corp.	College Point, N.Y.
American Smelting and Refining Co.	New York, N.Y.
Amplex Chemical Co. Inc.	New York, N.Y.
Anaconda Sales Company	New York, N.Y.
Anchor Alloy Inc.	Brooklyn, N.Y.
Anglo-American Metal & Ferro Alloy Corp.	New York, N.Y.
Atomergic Chemicals Co.	Carle Place, N.Y.
B & B Engineering Corp.	Norwood, La.
B & B Motor and Control Corp.	New York, N.Y.
J. T. Baker Chemical Co.	North Phillipsburg, N.J.
Belmont Smelting and Refining Works Inc.	Brooklyn, N.Y.
Bogue Electric Manufacturing Co.	Paterson, N.J.
Bradley Laboratories Inc.	New Haven, Conn.
Bradley Semiconductor Corp.	New Haven, Conn.
Cadillac Electric Products	New Rochelle, N.Y.
Ceramic Color and Chemical Manufacturing Co.	New Brighton, Pa.
Christie Electric Corp.	Los Angeles, Calif.
City Chemical Corp.	New York, N.Y.
Clinton Supply Co. Inc.	Chicago, Ill.
Darby Co. Ltd.	Pittsburgh, Pa.
Davidson Aluminum & Metal Corp.	Brooklyn, N.Y.
B. F. Drakenfield & Co.	New York, N.Y.
E. I. du Pont de Nemours & Co. Inc.	Wilmington, Del.
Ealing Corporation	Cambridge, Mass.
Edal Industries, Inc.	East Haven, Conn.
Electron Equipment Corp.	South Pasadena, Calif.
Electronic Devices Inc.	Brooklyn, N.Y.
Electronic Devices Inc.	Yonkers, N.Y.
Electronic Rectifier Co. Inc.	Rochester, N.Y.
Electro-Seal Corp.	Des Plaines, Ill.
Electronic Space Products	Los Angeles, Calif.
Fansteel Metallurgical Corp.	North Chicago, Ill.
Franklin Fibre-Lamitex Corp.	Wilmington, Del.
Gates Electronic Co. Inc.	Bronx, N.Y.

(continued)

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TABLE 9

LIST OF MERCHANDISERS AND CONSUMERS
OF SELENIUM AND ITS COMPOUNDS[116]

General Electric Co.	Schenectady, N.Y.
General Instrument Corp.	Hicksville, L.I., N.Y.
Green Electric Co. Inc.	Fair Lawn, N.J.
Industrial Metals Improvement Co.	Pittsburgh, Pa.
Industrial Rectifier Co.	New York, N.Y.
Insulation Products Co.	Pittsburgh, Pa.
International Rectifier Corp.	El Segundo, Calif.
IRC Inc., Boone Div.	Boone, N.C.
ITT Components Div.	Clifton, N.J.
Kawecki Chemical Co. Inc.	New York, N.Y.
Kennecott Sales Corp.	New York, N.Y.
Kneisley Electric Co.	Toledo, Ohio
La Marche Bros.	Chicago, Ill.
Lambda Electronics Corp.	Plainview, N.Y.
Ledex Div., Ledex Inc.	Dayton, Ohio
Lorain Products Corp.	Lorain, Ohio
Macarr Inc.	New York, N.Y.
McKesson & Robbins, Inc.	New York, N.Y.
Meaker Co.	Chicago, Ill.
Meaker Co.	Nutley, N.J.
Mellaphone Corp.	Rochester, N.Y.
Metallurgical Products Co.	Philadelphia, Pa.
Metropolitan Metal Co.	Detroit, Mich.
Miller Sanford Corp.	Brooklyn, N.Y.
Model Rectifier Corp.	Brooklyn, N.Y.
Ohio Semiconductors Division	Columbus, Ohio
Opad Electric Co. Inc.	New York, N.Y.
Pancoast International Corp.	New York, N.Y.
Phelps Dodge Refining Corp.	New York, N.Y.
Power Designs Inc.	Westbury, N.Y.
Radio Receptor Co. Inc.	New York, N.Y.
Ramm Rectifier Co. Inc.	New York, N.Y.
Ramyr Manufacturing Co.	Los Angeles, Calif.
Rapid Electric Co. Inc.	Bronx, N.Y.
Rectico Inc.	Cedar Grove, N.J.
Rectifier Engineering & Supply Co.	St. Louis, Mo.
Republic Chemical Corp.	New York, N.Y.
J. E. Robin Inc.	East Orange, N.J.
J. A. Samuel & Co.	New York, N.Y.
Sarkes Tarzian Inc.	Bloomington, Ind.
Schauer Manufacturing Co.	Cincinnati, Ohio
Semi Alloys Inc.	Mt. Vernon, N.Y.
Seneca Electric Co.	Detroit, Mich.
Siegel Chemical Co. Inc.	Brooklyn, N.Y.
Strong Electric Corp.	Toledo, Ohio

(continued)

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TABLE 9

LIST OF MERCHANDISERS AND CONSUMERS
OF SELENIUM AND ITS COMPOUNDS[116]

Sylvan Chemical Corp.	Englewood Cliffs, N.J.
Syntron Co.	Homer City, Pa.
Technical Apparatus Builders	New York, N.Y.
C. Tennant Sons & Co. Inc.	New York, N.Y.
Ther Electric & Machine Works Inc.	Chicago, Ill.
Trojan Rectifier and Equipment Co. Inc.	Lancaster, N.Y.
United Mineral & Chemical Corp.	New York, N.Y.
R. T. Vanderbilt Co. Inc.	New York, N.Y.
Westinghouse Electric Corp.	Pittsburgh, Pa.
Zenitherm Alloys Corp.	Elizabeth, N.J.
Max Zuckerman & Sons	Owings Mills, Md.

APPENDIX

TABLE 10 PROPERTIES, TOXICITY, AND USES OF SOME SELENIUM COMPOUNDS[75]

Compound	Properties	Toxicity	Uses
Aluminum selenide Al_2Se_3	Decomposes in water	May be irritating to eyes, mucous membranes. Causes garlic odor of breath, dizziness, nausea	In preparation of hydrogen selenide; in semiconductor research
Ammonium hydroselenate $NH_4(HSeO_4)$			
Ammonium magnesium selenate $Mg(NH_4)SeO_4$	Decomposes		
Ammonium selenate $(NH_4)_2SeO_3$	Decomposes		
Ammonium selenite $(NH_4)_2SeO_3$	Decomposed by heat	Occupational exposure has caused pallor, nervousness, depression, garlic odor of breath, gastrointestinal disturbances, and dermatitis	In manufacture of red glass as reagent for alkaloids
Antimony triselenide Sb_2Se_3	mp 605°C	Occupational exposure has caused pallor, nervousness, depression, garlic odor of breath, G.I. disturbances, and dermatitis	

(continued)

TABLE 10 PROPERTIES, TOXICITY, AND USES OF SOME SELENIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Arsenic hemiselenide As_2Se	Decomposes in boiling alkali hydroxide	Highly toxic. Causes pallor, nervousness, depression, garlic odor of breath and sweat, and G.I. disturbances	In manufacture of glass
Arsenic pentaselenide As_2Se_5	Decomposes when heated in air	Highly toxic. Causes pallor, nervousness, depression, garlic odor of breath and sweat, and G.I. disturbances	
Arsenic triselenide As_2Se_3	mp 260°C	Highly toxic. Causes pallor, nervousness, depression, garlic odor of breath and sweat, and G.I. disturbances	
Beryllium selenate $BeSeO_4$		Death may result from short exposure to incredibly low concentrations of element and its salts	
Bismuth selenide Bi_2Se_3	mp 170°C		In semiconductor research

(continued)

APPENDIX TABLE 10 PROPERTIES, TOXICITY, AND USES OF SOME SELENIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Cadmium selenate $CdSeO_4$	Decomposes at 100°C		
Cadmium selenide CdSe	mp 1350°C	Low toxicity because of insolubility	In photoconductors, semiconductors, photoelectric cells, and rectifiers; in phosphors
Calcium selenide CaSe			In electron emitters
Cesium selenate Cs_2SeO_4			
Chloroselenic acid $HClSeO_3$	mp 46°C		
Cupric hydroselenite $Cu(HSeO_3)_2$			
Cupric selenate $CuSeO_4$			In coloring Cu or Cu alloys black
Cupric selenide CuSe			As catalyst in Kjeldahl digestions; in semiconductors
Cupric selenite $CuSeO_3$			
Gold selenate $Au_2(SeO_4)_3$	Decomposes in light		

(continued)

APPENDIX

TABLE 10 PROPERTIES, TOXICITY, AND USES OF SOME SELENIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Gold selenide Au_2Se_3	Decomposed by heat		
Hydrogen selenide H_2Se	mp $-64^{\circ}C$	May be irritating to eyes, mucous membranes. Causes garlic odor of breath, dizziness, nausea	
Indium selenide InSe	mp $660^{\circ}C$		In semiconductor research
Lead selenate $PbSeO_4$	Decomposes		
Lead selenite $PbSeO_3$	Melts at about $500^{\circ}C$		
Lithium selenate $LiSeO_4$			
Lithium selenite $LiSeO_3$			
Manganese selenate $MnSeO_4 \cdot 2H_2O$			
Manganese selenide MnSe			
Manganese selenite $MnSeO_3 \cdot 2H_2O$			

(continued)

TABLE 10 PROPERTIES, TOXICITY, AND USES OF SOME SELENIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Phosphorus pentaselenide P_2Se_5	Decomposes		
Phosphorus triselenide P_4Se_3	mp 242°C		
Potassium biselenite $KHSeO_3$			
Potassium cobaltus selenate $K_2Co(SeO_4)_2$			
Potassium selenate K_2SeO_4			As reagent
Potassium selenide K_2Se			
Rubidium selenate Rb_2SeO_4			
Selenic acid H_2SeO_4	bp 260°C mp 58°C		
Selenium bromide Se_2Br_2	Decomposes at 227°C mp -46°C	Occupational exposure has caused pallor, nervousness, depression, garlic odor of breath, G.I. disturbances, and dermatitis	

(continued)

TABLE 10 PROPERTIES, TOXICITY, AND USES OF SOME SELENIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Selenium chloride Se_2Cl_2	Decomposes at 100°C bp 130°C mp -85°C	Can cause pallor, nervousness, depression, garlic odor of breath, depression, G.I. disturbances, and dermatitis	
Selenium disulfide SeS_2	mp 100°C	Occupational exposure has caused pallor, nervousness, depression, garlic odor of breath, G.I. disturbances, and dermatitis	In eczemas and fungus infections in dogs and cats
Selenium hexafluoride SeF_6	mp -39°C bp -34.5°C sublimes at -46.6°C	Occupational exposure has caused pallor, nervousness, depression, garlic odor of breath, G.I. disturbances, and dermatitis	As gaseous electric insulator
Selenium monosulfide SeS	Decomposes at 118-9°C	Occupational exposure has caused pallor, nervousness, depression, garlic odor of breath and sweat, G.I. disturbances, and dermatitis	Vet use: topically against eczemas, fungus infections, demodectic mange, flea bites in small animals

(continued)

APPENDIX

TABLE 10 PROPERTIES, TOXICITY, AND USES OF SOME SELENIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Selenium oxide SeO_2	mp 340°C	Occupational exposure has caused pallor, nervousness, depression, garlic odor of breath and sweat, G.I. disturbances, and dermatitis	In the manufacture of other selenium compounds; as a reagent for alkaloids
Selenium oxychloride $SeOCl_2$	bp 180°C	Strong irritant, vesicant. Can cause fatal pulmonary edema	
Selenium oxyfluoride $SeOF_2$	bp 124°C mp 4.6°C	Strong irritant, vesicant. Can cause fatal pulmonary edema	
Selenium tetrabromide $SeBr_4$	Decomposes at 70-80°C	Occupational exposure has caused pallor, nervousness, depression, garlic odor of breath, G.I. disturbances, and dermatitis	
Selenium tetrachloride $SeCl_4$	mp 305°C Sublimes at 170-196°C	Can cause pallor, nervousness, depression, garlic odor of breath, G.I. disturbances, and dermatitis	
Silver selenide Ag_2Se	mp 880°C		

(continued)

APPENDIX

TABLE 10 PROPERTIES, TOXICITY, AND USES OF SOME SELENIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Silver selenite Ag_2SeO_3	Decomposed by heat to selenium oxide		
Sodium hydroselenite $NaHSeO_3$			
Sodium selenate Na_2SeO_4			As insecticide in some horticultural applications
Sodium selenide Na_2Se	mp 875°C		
Sodium selenite Na_2SeO_3			In removing green color from glass during its manufacture as alkaloidal reagent
Stannic selenide $SnSe_2$	mp 650°C		
Stannic selenite $Sn(SeO_3)_2$			
Stannous selenide SnSe	mp 861°C		
Strontium selenate $SrSeO_4$			

(continued)

APPENDIX

TABLE 10 PROPERTIES, TOXICITY, AND USES OF SOME SELENIUM COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Strontium selenide SrSe			
Thallium selenate Tl_2SeO_4	mp 400°C		
Thallium selenide Tl_2Se	mp 340°C		
Zinc selenate $ZnSeO_4$	mp 50°C Decomposes		
Zinc selenide ZnSe	mp 1100°C	Occupational exposure has caused pallor, nervousness, depression, garlic odor of breath, G.I. disturbances, and dermatitis	

APPENDIX

TABLE 11

SELENIUM CONTENT OF DUST FROM AIR-CONDITIONING FILTERS, 1941[66]

Type of Building Where Sample Was Collected	Location	Se (ppm)
Industrial	Los Angeles, Calif.	0.8
Dry goods store	San Francisco, Calif.	0.05
Industrial	San Francisco, Calif.	0.6
Residence	Grand Forks, N.Dak.	6
Residence	Houston, Tex.	3
Residence	University City, Mo. (suburb of St. Louis)	2.5
Office building	St. Louis, Mo.	10
Unknown	Chicago, Ill.	2.5
Residence	Shaker Heights, Ohio (suburb of Cleveland)	2.5
Unknown	Philadelphia, Pa.	1.5
Office building	Washington, D.C.	5